VI.6 Advanced Fuel Cell Development

Objectives

- Evaluate DOE-sponsored SOFC systems.
- Measure response of SOFCs to coal contaminates and develop analysis tools to understand SOFC performance on coal syngas.
- Assess the dynamic performance of SOFC components and systems (e.g., hybrid and simple cycles), and determine control requirements for these advanced systems.
- Develop new coating methods for low-cost fuel cell metallic components.

Accomplishments

- Installed and operated the SECA Phase I prototype unit made by Delphi into the DOE Fuel Cell Test Facility to verify performance vs. SECA Phase I requirements.
- Measured the effect of hydrogen chloride, potentially one of the greatest (by volume) trace contaminate species after hydrogen sulfide, on SOFC performance, and developed detailed transport models to predict SOFC performance on coal syngas.
- Experimentally quantified the control response of hot and cold by-pass flows on hybrid operation, and obtained experimental validation of thermal gradient induced current recirculation within an SOFC cell following load loss.
- Advanced electrophoritic coating methods to allow application of manganese-cobalt and iron-nickel thin film coatings on SOFC metallic components.

Introduction

The U.S. DOE is supporting the development of solid oxide fuel cells through the Solid State Energy Conversion Alliance (SECA) program so that future coal-based power plants will achieve the highest possible fuel efficiency while protecting our environment. The goal of the SECA program is to provide low-cost fuel cell systems for multiple markets (e.g., stationary and automotive) as a stepping stone to low-cost coal-based plants. While several industry teams are currently developing SOFC systems for near-term markets, to achieve future coal-based operation will require new and innovative SOFC design and analysis tools, materials, and test and evaluation capability. The work performed here accomplishes all these by: 1) developing test capability for the evaluation of SOFC systems and components; 2) measuring the effects of coal syngas on cell performance; 3) applying advanced analysis tools for the purpose of understanding solid oxide fuel cell operation on coal syngas; and 4) developing low-cost manufacturing options for metal materials used in SOFCs.

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Approach

Systems Test and Evaluation Capability–Last year, the U.S. Department of Energy National Energy Technology Laboratory completed construction of a fuel cell test facility for evaluating the performance of prototype fuel cell systems developed by government sponsored fuel cell developers, Figure 1. The facility is configured to handle fuel cell systems running on natural gas or methane with a nominal power rating of 3 to 10 kW. As reported below, in FY 2007 this facility was used to evaluate two SECA prototype units.

Dynamic System and Component Studies–Both model and experimental studies are used to investigate the performance of fuel cell components and systems under real-world dynamic conditions. For systems studies, the focus is on hybrid systems, which is a key technology anticipated for future coal-based power plants. Here we employ a 'hardware-in-the-loop' approach whereby an experimental gas turbine is coupled to necessary hardware components (i.e., pipe volumes) that simulate the presence of a fuel cell via a real-time dynamic model. For component studies, the focus has been on fuel cell dynamics, and our approach is applying models to resolve conditions that exist when large load changes occur (events not commonly covered in the literature). Such conditions are of particular interest for SOFC operation given their relative sensitivity to increased thermal gradients that might arise, and it is important that models accurately predict the fuel cell response. In prior work, it was shown that these large transients induce conditions within the cell that result in current reversal, Gemmen and Johnson, (2005). To validate these results, this

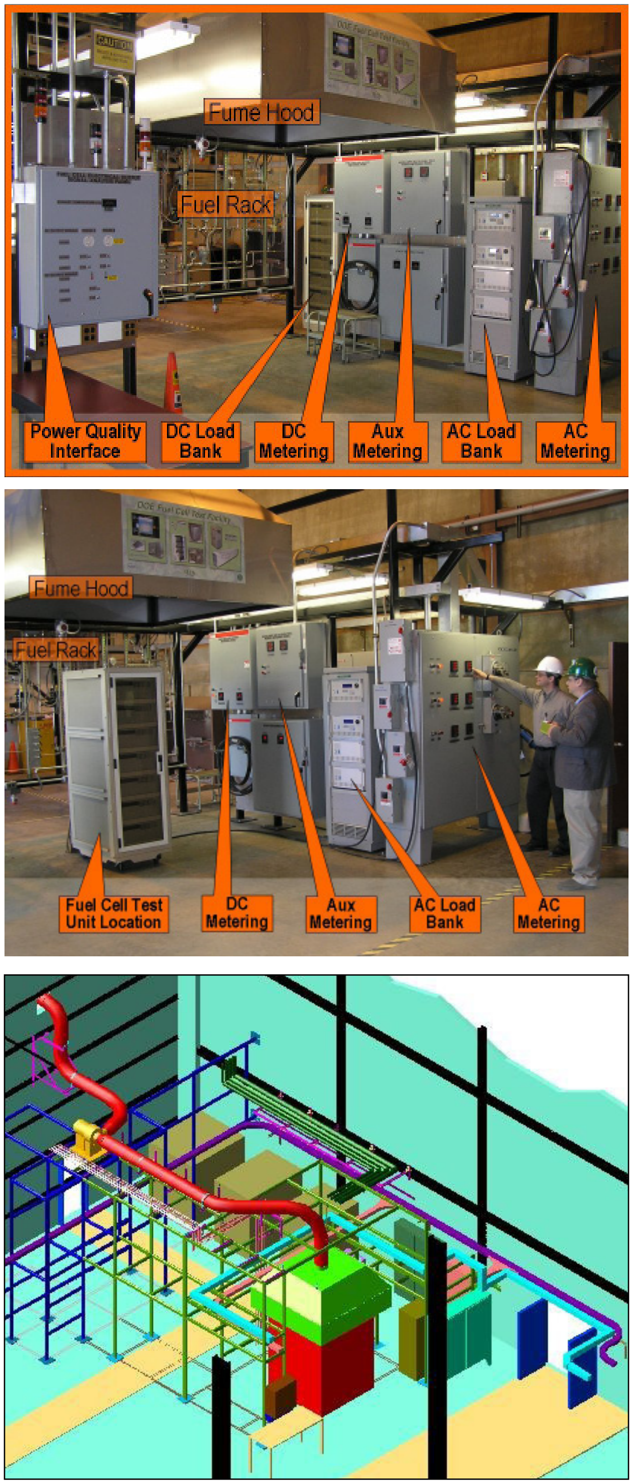

FIGURE 1. Photos and Layout of the DOE Fuel Cell Test Facility

project experimentally studied reverse current conditions induced by temperature variations.

Coal Syngas Operation–This year, we have begun investigating the effect of trace syngas elements (e.g., Cl, As, Cd, Hg, P) on SOFC operation. Our approach is to individually inject such elements in the forms that they exist under post syngas clean-up conditions into the fuel gas passing over an SOFC button cell. Because future cleanup systems have not been fully identified, these tests are performed over a range of temperatures and specie concentrations. Finally, plans are now under way to support a short term test at a U.S. gasification facility to directly assess SOFC operation on today's gasifier and cleanup technology.

Coatings for Metallic SOFC Components–There is a need to identify low-cost coating methods for the low-cost iron alloy steels used in SOFCs. The approach taken in this portion of our work is to investigate electrophoritic deposition methods. Such methods have an advantage in regards to their ability to deposit coatings on potentially intricate metallic components (components that have machined or stamped features to allow improved operation of the fuel cell). The goal of the tests performed this past year is to determine the proper liquid electrolyte compositions that provide the desired phase formations in the deposited coating. Systems studied thus far are Mn-Co and Fe-Ni coating systems.

Results

Systems Test and Evaluation Capability–This year, two SECA prototype units are to be independently tested by NETL. The first, by Delphi Corporation, has already completed testing, and analysis of the data is underway. Preliminary results show an average DC output efficiency of 31% over a 1-hour test. No measurable degradation (to within experimental resolution) was determined over the first 10-day portion of testing analyzed as of this writing. The second unit, by FuelCell Energy and Versa Power Systems Corporations, is currently being installed and testing should be completed by the end of the fiscal year.

Dynamic System and Component Studies–The hybrid simulation facility experimentally investigated the effect of cathode air bypass control on plant response. Two cases were investigated: (1) constant inlet temperature control via a combustor; (2) constant fuel input to the cathode inlet combustor. The work was published in the proceedings of the 2006 ASME Fuel Cell Conference, Tucker et al. (2006). Results showed that the initial plant response was due to fuel cell thermal energy output response which was lowered following a drop in cathode flow, Figure 2. As Figure 2 also shows, there is an immediate associated drop in turbine speed as well. This result was the same for both cases studied (albeit less for the case where fuel input was held fixed). The conclusion is that control of inlet combustor temperature cannot be used to manage short term changes in gas turbine response due to cathode air flow changes.

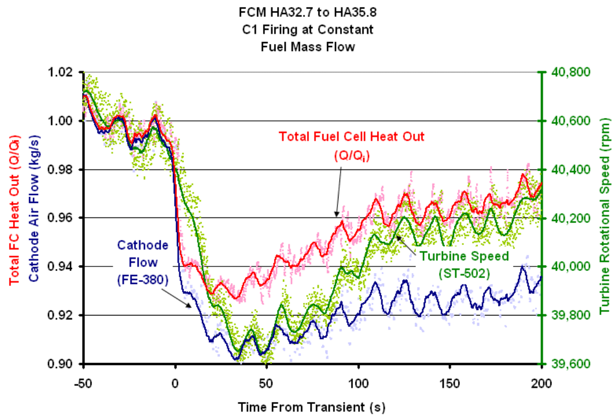

FIGURE 2. Cathode Air Inlet Flow, Turbine Rotational Speed and Total Fuel Cell Thermal Output Energy as a Function of Time Following Hot Air By-Pass Change

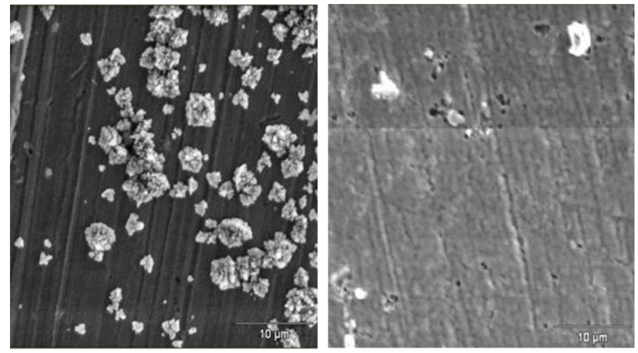

FIGURE 3. SEM images of deposits of Co on metallic substrates. The image on the left is of a deposit of Co from a simple solution of $CoSO_4$, and the image on the right shows the same deposition product, except that 0.0025M saccharin has been added to the solution.

Finally, regarding fuel cell component dynamic load studies, experimental results confirmed model predictions that show how thermal gradients result in internal current circulation upon loss of load, Gemmen et al. (2006). It is concluded that applications of models to study large load loss conditions, such as may be done to predict failure and degradation responses of fuel cells, will need to include electrolysis capability to achieve accurate predictions of the cell response.

Coal Syngas Operation–Both theoretical and experimental work has been performed to identify trace components that are reactive to nickel-based anodes. Because there is very little information regarding gas and solid phase components emitted from the gasifier and cleanup systems, detailed thermodynamic studies, using the FactSage software, were performed to guide the experimental work. Findings from the study showed that many of the trace species in the coal syngas will not likely interact with the SOFC anode. The elements Be, Cr, K, Na, V, and Z were all found to form condensed phase species under warm gas cleanup system conditions. Hence, it is likely that these species will not pose any great threat to SOFC anode operation except for potential gasifier/cleanup upset conditions. Finally, the thermodynamic evaluations showed that Sb, As, Cd, Hg, Pb, P, and Se vapor phase forms were found in the coal syngas at warm gas cleanup conditions which would allow the species to travel to the SOFC module and potentially interact with the SOFC anode. Hence, these components will be the focus of further thermodynamic and experimental work.

Coatings for Metallic SOFC Components–The electrophoritic research, Johnson et al. (2006) determined that saccharin addition to the deposition solution acts as a leveling agent, leading to much smoother films, Figure 3. It is also necessary to adjust the deposition potentials of the Mn/Co solution by complexation of the Co^{2+} ion with ethylenediamine tetraacetic acid (EDTA) and control of the Mn deposition species by adjusting the pH of the solution. In the case of the Ni/Fe solution, the relatively close standard reduction potentials for Ni and Fe means that chelation of the Ni^{2+} cation by EDTA suffices to adjust the deposition potential for the alloy solution. For the Mn/Co alloy deposition, it is important to take care not to drive the water splitting reaction so fast that localized pH levels cause hydroxide formation on the work piece. We have begun studying the oxidation process for the deposited alloys, and thus far spinel phases have been detected by x-ray diffraction after the alloy coated samples. It is not clear at this time what specific spinel has formed, and further analysis by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy will be accomplished.

Conclusions and Future Directions

The DOE Fuel Cell Test Facility has begun independently evaluating SECA prototype units, and will be providing results to the SECA Program Management for their evaluation and assessments regarding progress being made in meeting SECA goals. Two Phase I units were tested in FY 2006, and the remaining four units will be tested in FY 2007. Beginning in FY 2007, the major level of future work will be in investigating coal-based fuel cell systems, and in particular the effects of trace species on fuel cell operation. Tests for the effects of Sb, As, Cd, Hg, Pb, P, and Se based compounds on fuel cell performance remains to be completed. While these studies will be the main focus, we also anticipate the need to improve our understanding of these future coal-based systems via steady and dynamic modeling investigations in order to be assured that proposed hybrid systems will operate safely. Finally, progress is still needed to achieve low-cost metallic components suitable for SOFC conditions. Hence, continued work at developing low-cost coating methods will continue so that sufficiently dense and uniform thin film protective coatings, for both coal-based and non-coal-based SOFC systems, can be achieved.

Special Recognitions & Awards/Patents Issued

1. Best Paper Award–Cycle Innovation Committee of the ASME Turbo Expo. Shelton, M., I. Celik, I., E. Liese, D. Tucker, "A Study in the Process Modeling of the Startup of Fuel Cell/Gas Turbine Hybrid Systems," Paper No. GT2005-68466, ASME Turbo Expo 2005, Power for Land, Sea, and Air, June 6-9, 2005, Reno, NV.

FY 2006 Publications/Presentations

1. Gemmen, R., C. Johnson, "Effect of Load Transients on SOFC Operation–Current Reversal on Loss of Load," J. Power Sources, 144 (2005), pp. 152-164.

2. Gemmen, R., C. Johnson, "Thermal Gradient Induced Current Recirculation on Load Change in Solid Oxide Fuel Cells" Paper No. FUELCELL2006-97187, Proceedings of the Fourth International Conference on Fuel Cell Science, Engineering and Technology, June 19-21, 2006, Irvine, CA.

3. Gemmen, R., J. Trembly, "On the Mechanisms and Behavior of Coal Syngas Transport and Reaction within the Anode of a Solid Oxide Fuel Cell," submitted to J. Power Sources, 2006.

4. Johnson, C., R. Gemmen, C. Cross, "Alloy Films Deposited by Electroplating as Precursors for Protective Oxide Coatings on Solid Oxide Fuel Cells Metallic Interconnect Materials," to be presented at the Material Science and Technology Conference and Exposition, October 15-19, Cinergy Center, Cincinnati, OH.

5. Trembly, J.P., R.S. Gemmen, and D.J. Bayless, "The Effect of Coal Syngas with Hydrogen Chloride on the Performance of a Planar Solid Oxide Fuel Cell," 31st International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, May 21-25, 2006.

6. Trembly, J.P., R.S. Gemmen, and D.J. Bayless, "A Study of the Transport of Coal Syngas Species through a Solid Oxide Fuel Cell Anode," The 23rd International Pittsburgh Coal Conference, Pittsburgh, PA, September 25-28, 2006.

7. Tucker, D., L. Lawson, T. Smith, C. Haynes, "Evaluation of Cathodic Air Flow Transients in a Hybrid System Using Hardware Simulation," Paper No. FUELCELL2006-97107, Proceedings of the Fourth International Conference on Fuel Cell Science, Engineering and Technology, June 19-21, 2006, Irvine, CA.

8. Tucker, D., L. Lawson, J. VanOsdol, J. Kislear, A. Akinbobuyi, "Examination of Ambient Pressure Effects on Hybrid Solid Oxide Fuel Cell Turbine System Operation Using Hardware Simulation" Paper No. GT2006-91291, Proceedings of the ASME Turbo Expo 2006, May 8-11, 2006, Barcelona, Spain.

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1. Gemmen, R., C. Johnson, "Effect of Load Transients on SOFC Operation–Current Reversal on Loss of Load," J. Power Sources, 144 (2005), pp. 152-164.

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3. Tucker, D., L. Lawson, T. Smith, C. Haynes, "Evaluation of Cathodic Air Flow Transients in a Hybrid System Using Hardware Simulation," Paper No. FUELCELL2006-97107, Proceedings of the Fourth International Conference on Fuel Cell Science, Engineering and Technology, June 19-21, 2006, Irvine, CA.

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